DEVELOPMENT AND CHARACTERIZATION OF SULFONATED POLYETHERSULFONE FOR PROTON EXCHANGE MEMBRANE FUEL CELL APPLICATION

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ABSTRACT

Sulfonated polyethersulfone (SPES) with 20% concentration by weight were prepared with concentrated sulfonic acid at room temperature. Membrane solution developed in this study consisted of polyethersulfone dissolved in N,N – Dimethylformamide (DMF) as solvent, fuming sulfuric acid (36%) and concentrated sulfuric acid (95%-97%) as the sulfonating agent. The solution was cast manually at temperature between 25^{o}C-28 ^{o}C. The investigation on water uptake, TGA, CHNOS elemental analysis, and FTIR has been conducted. Successful introduction of the sulfonated groups was confirmed by using the FTIR spectra in the wave number range 1020cm^{-1}-1030 cm^{-1} which attributed to the symmetrical stretch of the sulfonated group. It was found that sulfonated membrane produced from mixed sulfonating agent (98% H_2SO_4 and 36% $H_2SO_4.SO_3$) have higher degree of swelling. The type and ratio of the sulfonating agent has been identified as one of the most influential parameter in determining the bonding of -HCO_3 as well as the membrane performance thus, producing different morphology. The parameter such as sulfonating agent ratio and type used strongly affects the membrane performance.

ABSTRAK

Polyethersulfone sulfonat (SPES) dengan konsentrasi mengikut berat sebanyak 20% telah disediakan dengan menggunakan asid sulfurik pekat pada suhu bilik. Cecair membran yang disediakan dalam kajian ini mengandungi polyethersulfone yang di larutkan didalam N,N-Dimethylformamide(DMF) yang bertindak sebagai pelarut, asid sulfurik wasap (36%), asid sulfurik pekat (95%-97%) sebagai agen pensulfonasian. Cecair membran diacu pada suhu bilik dan tekanan bilik.Kajian terhadap penyerapan air, TGA, CHNOS analisa dan FTIR kemudian dijalankan. Pengenalan kumpulan sulfonat kepada rantai utama telah disahkan menggunakan sinaran FTIR pada jarak sinaran 1020cm^{-1}-1030cm^{-1}. SPES-C dengan campuran asid sulfurik pekat dan asid sulfurik wasap sebagai agen pensulfonasian adalah paling larut kepada air dan mempunyai peratusan tertinggi untuk ujian tersebut. Dengan nisbah 1:2 (pekat:wasap), SPES-C adalah yang terbaik untuk ujian serapan air dan ini diikuti oleh SPES-B pada keadaan yang sama. Jenis dan nisbah agen pensulfonasian telah dikenal pasti sebagai salah satu factor utama dalam pengikatan HCO_3 begitu juga dengan prestasi lantas menghasilkan morfologi berbeza. Adalah dipercayai parameter seperti nisbah agen pensulfonasian dan jenis agen memberi impak besar kepada prestasi membran.

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Cp	-	heat capacity
Ft	-	feet
g/mol	-	gram per mol
hr/yr	-	hour per year
K	-	kelvin
Kg	-	kilogram
kg/hr	-	kilogram per hour
kg/kmol	-	kilogram per kilomol
kg/m3	-	kilogram per meter cubic
kJ	-	kiloJoule
km	-	kilometer
kmol/hr	-	kilomol per hour
m	-	meter
m3	-	meter cubic
ml	-	mililiter
ppm	-	parts per million
RM	-	ringgit Malaysia
s	-	second
sq	-	square
%	-	percentage
°C	-	degree Celcius
SPES	-	Sulfonated polyethersulfone
PES	-	Polyethersulfone

CHAPTER 1

INTRODUCTION

1.1 Background of study

Fuel cell represents a clean alternative to current technologies for utilizing hydrocarbon fuel resources. Polymer electrolyte membrane fuel call (PEMFCs) have acquired due to their importance as the best system for applications where a quick start up is required such as in automobiles. The prime requirement of fuel cell membranes are high proton conductivity, low methanol/water permeability, good mechanical and thermal per fluorinated ionomers, hydrocarbon and aromatic polymers and acid-base complexes. Although fuel cell are not a recent development, the use of polymeric membranes as electrolytes has received a tremendous impetus in the recent years and became the premiere candidate as a portable power source for small vehicles and buildings that replaces the rechargeable batteries(Georgi, 2005).

Polymeric membrane for fuel cell has been developed in recent years for wide range of industrial applications using porous and non-porous materials. The intrinsic properties of a material stem from its chemical structure as every single component have different structure that will determine its properties. All this chemical structures factors determines its basic mechanic properties, chemical resistance and permeability. The processing also affects in a certain way the properties because the morphology of the material obtained are related to the process by which the polymer was transformed. Therefore, there was a strong independence on the final properties between the polymer structure and elaboration conditions. The performances of fuel cell are known to be influence by many parameters including operating temperature, pressure and relative humidity of the gas stream etc. In this context, a membrane that complies with the basic requirement of fuel cells has been the principal goal of the research.

1.2 Problem statement

Although PES has excellent physical performance characteristic, the hydrophobicity of this material has limited its application sometimes. Sulfonation is a frequently used means for polymer modification to improve their membrane properties

1.3 Objectives

The objectives of this project are to develop a membrane based on polyethersulfone for the use of Proton Exchange Membrane Fuel Cell (PEMFC) that can adapt with the basic requirement of a fuel cell application.

1.4 Scope of Study

In order to meet the objectives, some scopes of studies are needed to be focused.

(i) Preparations of the sulfonated polyethersulfone solution and fabrication of sulfonated membranes.

(ii) Physical and chemical characterization of the produced sulfonated membranes.

CHAPTER 2

LITERATURE REVIEW

A fuel cell harnesses the chemical energy of hydrogen and oxygen to generate electricity without combustion or pollution. Fuel cell technology isn't new; NASA has used fuel cells for many years to provide power for space shuttles' electrical systems. In the near future, many vehicles may also be powered by fuel cells. Along the process of writing this literature review, a lot of fuel cell type will be introduced but the focused are more to the type of fuel cell typically used in automobiles that is the proton exchange membrane, also called a polymer electrolyte membrane fuel cell (Phair *et al*, 2001).

2.1 Fuel Cells

A new form of energy production has been in the works since the space race in the 1950's during the cold war between the Soviet and the United States of America. It's not eligibly introduced as a battery, but it practically isn't quite a combustion engine either. Fuel cells seem to be the wave of the future for electricity production. Some researcher even goes further and declared that no power generation system in the world one day can undo the efficiency of a fuel cell (Colleen, 2007).

2.1.1 History

The PEM fuel cell was first invented in the early 1960s, by Willard Thomas Grubb and Lee Niedrach of General Electric. Initially, sulfonated polystyrene membranes were used for electrolytes, but then were replaced in 1966 by Nafion ionomer. This new type of membranes proved to be superior in performance and durability to sulfonated polystyrene. PEM fuel cells were used in the NASA Gemini series of spacecraft, but they were replaced by Alkaline fuel cells in the Apollo program and in the Space shuttle Parallel. Pratt & Whitney Aircraft, General Electric developed the first proton exchange membrane fuel cells (PEMFCs) for the Gemini space missions in the early 1960s. The first mission to utilize PEMFCs was Gemini V. This had been since, become the turning point for the used of fuel cell.

Extremely expensive materials were used and the fuel cells required very pure hydrogen and oxygen. Early fuel cells tended to require inconveniently high operating temperatures that were a problem in many applications. However, fuel cells were seen to be desirable due to the large amounts of fuel available.

Despite the success in space programs, fuel cell systems were limited to space missions and other special applications, where high cost could be tolerated. It was not until the late 1980s and early 1990s that fuel cells became a real option for wider application base. Several pivotal innovations, e.g. low platinum catalyst loading and thin film electrodes drove the cost of fuel cells down, making development of PEMFC systems more realistic. However, there had been significant debate as to whether hydrogen fuel cells will be a realistic technology for use in automobiles or other vehicles (Bocarsly, 2002).

2.1.2 Fuel Cell Construction

Electricity are nothing more than flowing electrons. That means that power generation are nothing more than finding out how to free electrons. Fuel cells rely on hydrogen for its electrons. There are many different fuel cells for every kind of application. But every fuel cell has the same essentials. Each fuel cell have an anode (negative electrode) comprised of hydrogen gas, and a cathode (positive electrode) of oxygen. In the middle are electrolytes that only allow protons to pass through it. In between both electrodes and the electrolyte are catalysts that facilitate the reactions (Colleen, 2007).

2.1.3 The Chemistry of Fuel Cells

The fuel cell basically works by injecting molecular hydrogen (H_2) molecules into the anode. These are to allow the hydrogen molecules to react with the catalyst. The catalysts used are usually a thin coat of powdered platinum on carbon paper. The function of the catalyst was to break the hydrogen into a proton and an electron. The proton goes across the electrolyte, while the electrons are fed through the circuit and goes to work, and that creating electric power. Upon finishing this process, the electrons return to the cell through the cathode. There, the catalyst assists the oxygen molecules, the hydrogen protons and the hydrogen electrons in making water. The chemical reactions are as follows:

Anode:

$$2H_2 \rightarrow 4H_+ + 4e- \qquad 2.1$$

Cathode:

$$O_2 + 4H_+ + 4e- \rightarrow 2H_2O \qquad 2.2$$

The whole reaction ends up looking like this:

$$2H_2 + O_2 \rightarrow 2H_2O \qquad 2.3$$

This reaction only creates about 0.7 volts. These powers produced are still considered as small compared to the power that will be used to generate something as big as a car. Because of this, there are several cells built into a stack. This multiplies the voltage up to useable levels (Katsura, *et al*, 2008).

2.1.4 Types of Fuel Cells

The most important parts in fuel cells are electrolyte. Different electrolytes provide different voltages and different properties. The fuel cells destined to appear under car hoods are called a Proton Exchange Membrane Fuel Cell. The stacks that will be used to fuel the car are about the size of an average sized printer.

Other fuel cells are much bigger (ranging in size from a large central air conditioning unit to a compact car.) These cells are stationary and can provide electricity to an apartment complex, an office building or 60 family homes. The types of fuel cell are:

2.1.4.1 Phosphoric Acid Fuel Cell (PAFC)
2.1.4.2 Molten Carbonate Fuel Cell (MCFC)
2.1.4.3 Solid Oxide Fuel Cell (SOFC)
2.1.4.4 Alkaline Fuel Cell (AFC)
2.1.4.5 Proton Exchange Membrane Fuel Cell (PEMFC)

All of these fuel cells are large and take a relatively long time to heat up (or "prime the hydrogen pumps") which became the reason why they are not suitable for automobiles. These large-scale fuel cells operate at high temperatures as well, (they range from about 1,000° F to 1,800° F) which allows engineers another way of producing energy. The heat from the fuel cells can be used to boil water (perhaps the water it produces) and turn steam turbines for even more electricity.

2.1.4.1 Phosphoric Acid Fuel Cell (PAFC)

PAFC are the most developed fuel cell technology applied for power stations installed in buildings, hotels, hospitals and electric utilities in countries such as Japan, United States and European country. These types of fuel cell uses liquid acid as its electrolytes contains in silicone carbide matrix. These systems work at temperature higher than PEMFC or alkaline fuel cells yet still require platinum catalyst on the electrodes to promote reactivity. The anode and cathode reactions are same as any fuel cell system but it occur at a faster rate system due to the higher operating temperature (Weaver, 2002).

The efficiency of this system was proven to be lower than any of the fuel cell system, at around 40%. It also took longer time to warm up compared to PEMFC. Despites the lack of efficiency and warm up time, there are also advantages included in the system such as simple construction, stability, and lower electrolyte volatility.

Nowadays, the cost of the PAFC plant, which cost about US $ 3500 per KW, has appeared to be severe limitations for the widespread use and it seems that the possibilities for further technology improvements on such technologies are out of questions.

2.1.4.2 Molten Carbonate Fuel Cell (MCFC)

MCFC use either lithium sodium carbonate or molten lithium potassium as the electrolyte. The high temperature at which these cells operate means that they are able to internally reform hydrocarbons, such as natural gas and petroleum, to generate hydrogen within the fuel cell structure (Weaver, 2002).

2.1.4.3 Polymer electrolyte membrane fuel call (PEMFCs)

Polymer electrolyte membrane fuel call (PEMFCs) have acquired due importance as they are the best for applications where a quick start up is required such as in automobiles. The prime requirement of fuel cell membranes are high proton conductivity, low methanol/water permeability, good mechanical and thermal per fluorinated ionomers, hydrocarbon and aromatic polymers and acid-base complexes. Although fuel cell are not a recent development, the use of polymeric membranes as electrolytes has received a tremendous impetus in the recent past and became the premiere candidate as portable power source for small vehicles and buildings that replaces the rechargeable batteries.

Polymeric membrane for Fuel Cell has been developed in recent years for wide range of industrial applications using porous and non-porous materials. The intrinsic properties of a material stem from its chemical structure as every single component have different structure that will determine its properties. All this chemical structures factors determines its basic mechanic properties, chemical resistance and permeability. The processing also affects in a certain way the properties because the morphology of the material obtained are related to the process by which the polymer was transformed. Therefore, there was a strong independence on the final properties between the polymer structure and elaboration conditions.

The performances of fuel cell are known to be influence by many parameters including operating temperature, pressure and relative humidity of the gas stream etc.

A proton exchange membrane fuel cell transforms the chemical energy liberated during the electrochemical reaction of hydrogen and oxygen to electrical energy, as opposed to the direct combustion of hydrogen and oxygen gases to produce thermal energy.

Streams of hydrogen were delivered to the anode side of the membrane electrode assembly (MEA). At the anode side it was catalytically split into protons and electrons. This oxidation half-cell reaction is represented by:

$$2H_2 \rightarrow 4H + 4e \qquad 2.4$$

The newly formed protons permeate through the polymer electrolyte membrane to the cathode side. The electrons travel along an external load circuit to the cathode side of the MEA, thus creating the current output of the fuel cell. Meanwhile, a stream of oxygen is delivered to the cathode side of the MEA. At the cathode side oxygen molecules react with the protons permeating through the polymer electrolyte membrane and the electrons arriving through the external circuit to form water molecules. This reduction half-cell reaction is represented by

$$O_2 + 4H + 4- \rightarrow 2H_2O \qquad 2.5$$

2.1.5 Applications of Fuel Cells

Fuel cells have the potential to slip into various kinds of electronic devices. A few applications could include:

(i) Cars, as stated before, fuel cells the size of a printer could provide enough juice to power as well (if not better than) a combustion engine. Slightly larger units are already in place in several bus systems across the United States. The hydrogen for both forms of transportation may be provided through propane, methanol or natural gas.

(ii) Personal devices (laptops, cell phones, and hearing aides) fuel cells have the tremendous potential to get into every electronic device we come in contact with. Fuel cells offer the possibility of laptops and cell phones with energy life measured in days or weeks, rather than hours. The fuel cell is scalable, which means it can go small enough to power medical devices that normally require battery replacement.

(iii) Stationary power production and backup- larger-scale fuel cells could allow every city to have its own power station, rather than a centralized power grid. Power generation could become so decentralized that each housing development or apartment complex could be self-sustained with its own power. This would drastically cut down on pollution and ugly power lines. Hospitals and airports could (some already do) have backup power supplies that kick in, in the event of a power failure.

2.2 Membrane

Membrane science and technology are expending each and every day and without any doubt are becoming a prominent part of many activities within the process industry and power generation industry. This however does not justify with the wide fields of separations in which membranes are used.

The word separation conjures up a model of removing one component or species from a second component, for example a mass transfer process such as distillation. Separation in synthetic membranes has put the terminology separation in a wider context. A range of separation of the chemicals/mass transfer type have developed around the use of membranes including distillation, extraction, absorption, adsorption, and stripping, as well as separations of the physical type such as filtration. Synthetic membranes are an integral part of a device for analysis, energy generation and cells in the electrochemical industry.

Membrane technologies are in a state of rapid growth and innovation since the history of 40 years ago and becoming more active in the last decades. The world has watch numerous different separation processes have emerged in which synthetic membranes play a prominent role. Membrane separations are now routinely replacing separations which are unfortunately still referred as traditional. Go for a walk inside the research laboratory of many universities and industries to see membrane-based units supplying purified water (Jose Carlos *et al*, 2002).

A membrane are permeable or semi permeable phase, often a thin polymeric solid, which restrict the motion of certain species. These added phases are essentially function as a barrier between the feed stream for separation and one product stream. This barrier controls the relative rates of transport of various species through itself and thus, as with all separations, gives one product depleted in certain components and a second product that is concentrated in these components. The performance of a membrane had always been defined in few simple factors. It is defined as:

(i) Flux or permeation rate; the volumetric (mass or molar) flow rate of fluid passing through the membrane per unit area of membrane per unit time
(ii) Selectivity ; for solutes and particulates in liquids and gases ; retention are the fraction of solute in the feed retained by the membrane

(iii) Selectivity; for mixtures of miscible liquids and gases; Separation factor are the ratio of the concentration in the permeate divided by that in the feed for two components.

The uses to which membranes can be put are varied and include the separation of mixtures of gases and vapors, miscible liquids (organic mixtures and aqueous/ organic mixtures) and solid/liquid and liquid/liquid dispersion and dissolved solids and solutes from liquids. Thus virtually all separation requirements in industry can, in principle, be achieved with membranes. The main uses of membranes in industry are as the following areas:

(i) The filtration of micron and submicron size suspended solid (and dispersed liquid) from liquid and gases containing dissolved solid.
(ii) The removal of macromolecules and colloids from liquids containing ionic species.
(iii) The separation of mixtures of miscible liquids.
(iv) The selective separation of gases and vapors from gas and vapors from gas and vapors streams.
(v) The selective transport of ionic species only.
(vi) The virtually complete removal of all material, suspended and dissolved, from water.

The technical advantages of membrane separations which result in economic advantages are that they frequently achieve higher efficiency of separation, they often yield faster separations and the simplicity of operation in modern compact modules means operation with small or large plant are relatively easy.

Membrane technology has more recently been applied commercially to separate individual components from mixtures of liquids and gases, (area 3 and 4 above). The membranes here are non porous thin layers on porous substrates. The technical breakthrough, in terms of selectivity and rate of separation, in the membrane separation of gases had made has permeation competitive with cryogenic separation, adsorption, absorption, etc. Pervaporation are membrane process which can essentially replace fractionation by distillation, although applications are restricted to the more difficult separations which typically involve azeotrope formation such as ethanol/water. These processes are somewhat unique within membrane separation involving a change in phase from feed (liquid) to permeate (vapor).

The final mentioned for liquid-based separations, which removes ions selectivity, are called electrodialysis. Market areas are again similar to the membrane filtrations with a principle application in the desalination of brackish water. The economic advantages gained by electrodialysis are through its specificity and efficiency of separation of separation achieved at low temperatures. A major application of electrodialysis-type membranes (ion exchange) are as electrolyte call separation (Keith, 1998).

2.2.1 History membrane

In 1850, separate papers appeared in the *Journal of the Royal Agricultural Society of England* by agriculturist Sir H.S.M. Thompson and chemist J.T. Way. Researches describe the phenomenon of ion exchange as it occurs in soils. In that paper, the researches addressed to the question of how soluble fertilizers like potassium chloride were retained by soils even after heavy rains. The Experiment took a box with a hole in the bottom, filled it with soil, and poured onto the soil a solution of potassium chloride, collecting the liquid that flowed out of the bottom. The soil was then washed with rainwater and analyzed, from both the solution and the rainwater. The water turned out to contain all of the chloride that had been originally added but none of the potassium; the potassium had been replaced by chemically equivalent amounts of magnesium and calcium. Researchers called the process “base exchange” because of the basic (nonacidic) character of the exchanged elements. That term persisted until after

1940, by which time the process had become universally known as ion exchange (Wang *et al*, 1998).

In modern days, the process would be described in the following way: potassium ions enter the soil and displace calcium and magnesium ions. The chloride ions have no part in the operation and pass through unchanged. In terms of a chemical equation, the process is

$$2K^{+} + Ca^{2+}\ (soil) \rightleftharpoons Ca^{2+} + 2K^{+}\ (soil), \qquad 2.6$$

in which the double arrow indicates that the exchange was reversible. In Way's experiment, the process was pushed to completion because the water trickling through the soil continually came in contact with fresh calcium-loaded soil. As Way also observed, the potassium could be regained by washing the soil with a solution of calcium chloride (Hann, *et al*, 1990).

2.2.2 Membrane classification

The membrane, clearly the most important part of the separation process. This membrane material had been developed over the recent years to produce wide range of materials with different in structure and ways of functioning. Tables 2.1 regroup the types and properties of some synthetic membranes for technical interest. All these materials were generally classified into:

(i) Synthetic polymers; a vast source in theory although silicone rubbers, polysulphones, polyamides are prominent
(ii) Modified natural products; cellulose-based
(iii) Miscellaneous; include inorganic, ceramic, metals, liquid and dynamic membranes

The functioning of a membrane will depend on its structure as this essentially determines the mechanism of separation and thus the application. There are currently two types of structure generally found in membranes. It was symmetric and asymmetric. Symmetric membranes have three general types; with approximate cylindrical pores, porous and non porous. Asymmetric membranes are characterized by a non-uniform structure comprising of an active top layer supported by a sub layer. There are also divided into porous, porous with top and composites (Scott, 1998).

Table 2.1: Type, structure and preparation of synthetic membrane

Membrane type	Membrane structure	Preparation	Applications
Asymmetric CA,PA,PS,PAN	Homogenous or microporous, skin on a miroporous substructure	Casting and preparations	UF and RO, (MF) GP,PV
Composite CA,PA,PS, PI	Homogenous polymer film on a miroporous substructure	Deposition on microporous substructure	RO, GP, PV
Homogenous S	Homogenous polymer film	Extrusion	GP
Ion exchange DVB, PTFE	Homogenous or microporous copolymer film with positively or negatively charged fixed ions	Immersion of ion exchange powder in polymer, or sulphonation an amination of homogenouspolymer film	Ed
Microporous: Ceramic, metal glass	0.05-20 micrometer pore diameter 10-100 micrometer pore diameter	Moulding and sintering Leaching from two-component glass mixture	F(molecular mixtures)
Microporous: Sintered polymer PTFE,PE,PP	0.1-20 micrometer pore diameter	Moulding and sintering	F(suspensions, air filtration)
Microporous: Stretched polymer PTFE,PE	0.1-5 micrometer pore diameter	Stretching a partial crystalline film	F(air,organic solvents)
Microporous: Track-etched PC, PEsT	0.02-20 micrometer pore diameter	Irradiation and acid leaching	F(Suspension, Sterile filtration)
Symmetric microporous phase inversion CA	0.1-10 micrometer pore diameter	Casting and precipitation	Sterile filtration, water purification,dialysis

PTFE –polytetrafluoroethylene, CA-Cellulosic esters, PVC-Polyvinylchloride PA-polyamide
PE-Polyethylene, PS-Polysulfone, PP-Polypropylene, S-Silicon rubber,
PC-Polycarbonate, PEsT-Polyester PAN-polyacrylonitrile, PI-Polyamide,
DVB-divinylbenzene, UF-Ultrfiltration, RO-Reverse osmosis, GP-gas permeation,
MF-Microfiltration ED-electrodialysis, F-filtration, PV-Pervaporation